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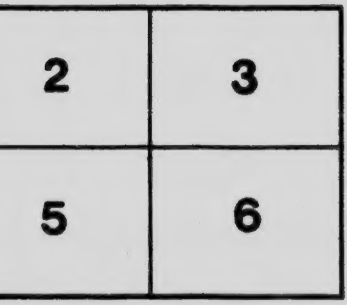

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PAPERS FROM THE PHYSICAL LABORATORIES

No. 31: THE ACTION OF ELECTROLYTES ON COPPER COLLOIDAL SOLUTIONS, BY E. F. BURTON

(Reprinted from The Philosophical Magazine, Series VI., Vol. 17)

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From the PHILOSOPHICAL MAGAZINE *for April* 1909.

The Action of Electrolytes on Copper Colloidal Solutions. *By* E. F. BURTON, *B.A., Demonstrator in Physics, University of Toronto* *.

1. INTRODUCTION.

THE problem of the effect of the presence of very small traces of electrolytes on the stability of colloidal solutions is one of the most important unsolved questions relating to colloids. The recent paper by Jacques Duclaux † tends to throw doubt on the theory of the isoelectric point first suggested by Hardy ‡; while a later contribution by Lottermoser § dealing with Duclaux's results shows, at least, that we have yet much to learn regarding the interaction of the colloidal particles and the dissolved salts.

The experiments detailed in the present communication are a continuation of those performed by the writer ‖ on the action of small traces of electrolytes on silver and gold colloidal solutions prepared by Bredig's method. In this former work it was found that, as minute quantities of aluminium sulphate were added in increasing amounts to either silver or gold solutions, the velocities with which the particles moved in a given electric field were at first reduced to zero and then reversed. As the particles in each case were negatively charged in the pure solution, according to Hardy's theory, the positively charged aluminium ions, and not the negatively charged sulphate ions, are the active ones in bringing about the discharge of the particles. It was further found that, not only was the charge of the particles reversed, but at the point where the charge was zero, *i. e.* at the point when the particles did not move in the electric field (Hardy's isoelectric point), the solutions showed a minimum stability. For example, to refer to a table taken from the former paper, two samples of a gold solution to which were added respectively 19×10^{-6} and 38×10^{-6} grm. of aluminium per 100 ccs. coagulated at the end of a few hours, while another sample of the same solution, to which 63×10^{-6} grm. per cc. were added, did not completely coagulate at the end of four days. As a result of this work we have strong evidence as to the validity of the assumption that, in these solutions at least, coagulation is brought about through the discharge of the colloidal particles by the ions of the electrolyte introduced into the colloidal solution, and that the deportment of the Bredig metallic colloidal solutions is similar to that which Hardy found displayed by his specially treated albumen solutions.

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* Communicated by Professor J. C. McLennan.

† *Jour. de Ch. phys.* vol. v. 1-2-3, p. 29.

‡ Proc. Roy. Soc. vol. lxvi. p. 110; Jour. of Physiol. vol. xxix. p. 26.

§ *Zeits. für phys. Chem.* vol. lx. 4, p. 451.

‖ Phil. Mag. ser. 6, vol. xii. Nov. 1906.

TABLE I.

Gold Colloidal Solution.

No.	Grms. Al added per 100 ccs. sol.	Specific Conductivity at 18° C.	Velocity of the particles in cms./sec./volt/cm.
1.	0	$3{\cdot}6 \times 10^{-6}$	* -33×10^{-5}
2.	19×10^{-6}	$5{\cdot}2 \times 10^{-6}$	$-17{\cdot}1 \times 10^{-5}$
3.	38×10^{-6}	$6{\cdot}6 \times 10^{-6}$	$+1{\cdot}7 \times 10^{-5}$
4.	63×10^{-6}	$11{\cdot}6 \times 10^{-6}$	$+13{\cdot}5 \times 10^{-5}$

* In this table, as in all succeeding ones, the + sign denotes motion toward the cathode, the − sign toward the anode.

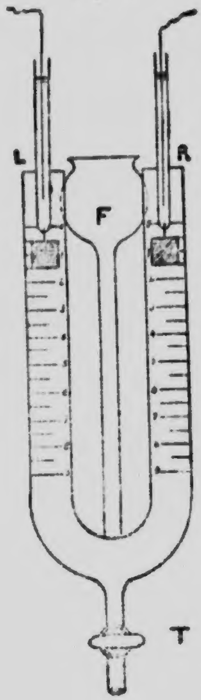
2. PURPOSE OF THE EXPERIMENTS.

The results given below may be viewed as an instalment of a systematic investigation on the effect of various electrolytic solutions on the velocities of colloidal particles in an electric field, and consequently the effect on the size and sign of the charge possessed by those particles. Copper colloidal solution has been selected because its particles are positively charged, *i.e.* the copper particles move to the cathode in the solution; in other words, they are charged oppositely to those of the silver and gold solutions worked with formerly.

The major part of the paper will deal with, firstly, the effect of solutions of two salts having the same acid radical and, respectively, a monovalent and a trivalent metal, viz., potassium sulphate and aluminium sulphate; and, secondly, with the effect of solutions of salts having the same metal ion and, respectively, monovalent, divalent, and trivalent acid radicals, viz., potassium chloride, potassium sulphate, potassium phosphate, and potassium ferricyanide. The results of these experiments fit in remarkably well with the theory first suggested by the work of Picton and Linder [*] and of Hardy [†], and supported by the conclusions drawn from analogous experiments on silver and gold solutions.

3. Experimental Work.

Fig. 1.



The solutions of copper were easily prepared according to Bredig's method by sparking with copper wires under the surface of conductivity water, the specific conductivity of which was usually about 2×10^{-6}. Using a current of from 5 to 6 amperes at a voltage of 110, 250 ccs. could be produced in a short time. The resulting solution was a very clear yellowish-brown liquid in which the particles remained suspended, apparently unchanged, for months. Several samples were made, the average copper content being ·0088 grm. per 100 ccs.

The velocity with which the particles moved in an electric field was measured by the U-tube method (see fig. 1) described in a former paper [‡]. Usually about 250 ccs. of the solution sufficed to carry out one series of experiments, and as each series was completed a fresh stock of solution was made from the same pieces of copper. In every case the velocity of the particles in the pure solution was found; the results of these observations are collected in Table II.

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[*] Jour. Chem. Soc. vol. lxi. p. 148; vol. lxvii. p. 63; vol. lxxi. p. 568.

[†] *Loc. cit.*

[‡] Phil. Mag. ser. 6, vol. xi., April 1906.

TABLE II.
Pure Copper Colloidal Solutions.

No.	Date of preparation.	Date of measurement of velocity.	Specific Conductivity at 18° C.	Velocity at 18° C.
1.	June 19, 1907	June 20, 1907	$7{\cdot}7\times10^{-6}$	$+23{\cdot}4\times10^{-5}$
2.	„ 20, 1907	„ 26, 1907	$6{\cdot}5\times10^{-6}$	$+25{\cdot}4\times10^{-5}$
3.	„ 5, 1908	„ 5, 1908	$8{\cdot}2\times10^{-6}$	$+24{\cdot}9\times10^{-5}$
4.	„ 16, 1908	„ 17, 1908	$5{\cdot}8\times10^{-6}$	$+25{\cdot}4\times10^{-5}$
5.	„ 23, 1908	„ 24, 1908	$4{\cdot}3\times10^{-6}$	$+30{\cdot}4\times10^{-5}$
6.	„ 27, 1908	„ 29, 1908	$3{\cdot}1\times10^{-6}$	$+33{\cdot}0\times10^{-5}$

For solutions Nos. 5 and 6 it will be noticed that the velocities are rather larger than for the others, but it will be seen that the specific conductivities of these solutions are also much lower than those of the others; that is to say, these latter two solutions were freer from electrolytes than the others, and, as we shall see, the general effect of added electrolytes is to reduce the velocity of the particle.

Although the velocities are all given at 18° C., the experiments were not performed at precisely that temperature, but corrections have been introduced to bring each reading to that standard temperature. In the paper * referred to above the following relation has been deduced as holding between the velocity (v) and the coefficient of viscosity of the liquid medium (μ):

$$\mu \,.\, v = \text{a constant},$$

as long as one deals with the same material in the particle and the same liquid medium. That this is in accord with the actual facts is confirmed by the following series of velocity determinations carried out with a silver colloidal solution at the temperatures indicated in Table III. The whole velocity tube was lowered into a glass thermostat which could be kept at the required temperature.

A fundamental necessity for the validity of velocity results obtained in this way, is that the specific conductivity of the superincumbent layers of water should be the same as that of the colloidal solution at the bottom of the tube. As these conductivities in each case were made equal at the ordinary temperature of the room before the liquids were introduced into the

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* Phil. Mag. ser. 6, vol. xi., April 1906.

TABLE III.

Silver Colloidal Solutions.

No.	Temperature Centigrade.	Velocity (v).	Viscosity of water (μ) at given temperature.	Product.
1.	3°	$15{\cdot}1\times10^{-5}$	·016214	$24{\cdot}5\times10^{-7}$
2.	9·9	$18{\cdot}6\times10^{-5}$	·013300	$24{\cdot}7\times10^{-7}$
3.	11	$19{\cdot}6\times10^{-5}$	·012822	$25{\cdot}1\times10^{-7}$
4.	21	$25{\cdot}3\times10^{-6}$	·009922	$25{\cdot}0\times10^{-7}$
5.	31	$30{\cdot}1\times10^{-6}$	·007972	$24{\cdot}0\times10^{-7}$
6.	40·5	$37{\cdot}2\times10^{-6}$	·006577	$24{\cdot}5\times10^{-7}$

velocity tube, evidently, in order that the results in Table III. may be of value, the temperature coefficients of the two liquids should be the same. These coefficients were compared for a sample of silver colloidal solution and a quantity of water of very nearly the same initial conductivity. The values of the resistances of these liquids at various temperatures are recorded in Table IV. and illustrated by the curves in fig. 2. From these we may safely conclude that the temperature coefficient of the resistance of colloidal silver solution is that of water itself.

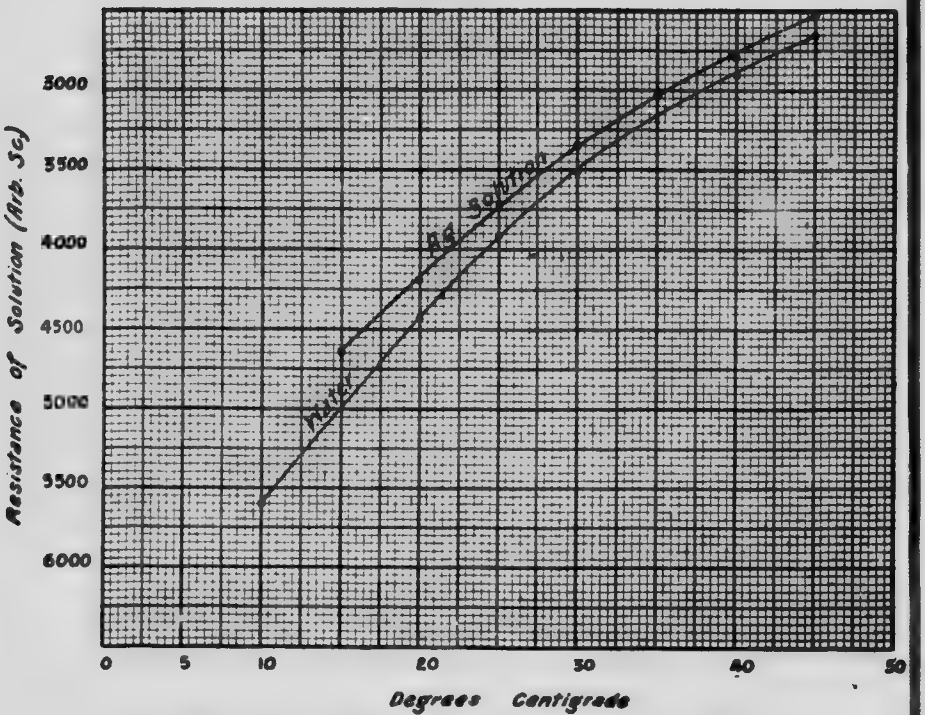
TABLE IV.

Temperature Coefficients of Resistance.

Temperature (Cent.).	Resistance of water (Arb. Sc.).	Resistance of Ag Sol. (Arb. Units.)
10°	5600	
15	......	4640
20	4420	4180
25	3910	3720
30	3510	3350
35	3150	3030
40	2900	2790
45	2660	2520

It is quite justifiable to apply these results for silver solutions to the manifestly analogous solutions of the other metals in water, in particular to the copper solutions now under consideration.

Fig. 2.



With each of the salts named in the foregoing section the procedure was the same. Solutions of the salts of determined normality were prepared with the conductivity water, and the amount of such solution added to a given quantity of colloidal solution was measured by counting drops as they came from a fine burette. The tap of the burette was turned so that the liquid dropped at a convenient rate, the number of drops given by 2 ccs. of the liquid was counted, a required number of drops was allowed to fall into the chosen amount of colloidal solution, and finally the number of drops in 2 ccs. was counted again with the tap still turned as at the beginning; the two calibrations always agreed, the burettes giving from 24 to 30 drops per cc. The burettes were always washed with distilled water and, just before being used for any solution, were rinsed with the latter several times. One was thus enabled to introduce into a given amount of colloidal solution a very exact, small quantity of a given electrolytic solution.

4. RESULTS.

A typical series of experiments on the effect of each of the electrolytes was as follows:—The velocity of the particles in the pure copper solution was first taken; gradually increasing quantities of the chosen electrolytic solution were then added to fresh samples of the stock copper solution and the corresponding velocity measured each time. The measurement of one velocity was completed usually within one hour of the addition of the electrolyte. All of the salts used were Kahlbaum's purest and were not specially re-tested.

a. *Potassium Chloride.*

In Table V. the velocities corresponding to the various amounts of this salt are given. Column 1 gives the number of grams of Cl (as KCl) per 50 ccs. of colloidal solution, a $\frac{N}{100}$ ($\frac{1}{100}$ grm.-mol.) solution of KCl being added drop by drop; column 2 gives the specific conductivity of the mixture in each case. In the next column the velocities of the particles (in cms. per sec. per volt per cm.) are written, the positive sign indicating that the motion of the colloidal particle was toward the cathode. In each table are included particulars as to the coagulation caused in each case.

TABLE V.

KCl added to Copper Colloidal Solution.

No.	Grams of Cl per 50 ccs. Cu Sol.	Spec. Cond. at 18° C.	Velocity at 100° C.	Coagulation.
1...... ...	0	$8{\cdot}2\times10^{-6}$	$+24{\cdot}9\times10^{-5}$	
2.........	$3{\cdot}0\times10^{-5}$	$11{\cdot}7\times10^{-6}$	$+25{\cdot}7\times10^{-5}$	No sign.
3.........	$6{\cdot}8\times10^{-5}$	$15{\cdot}3\times10^{-6}$	$+26{\cdot}2\times10^{-5}$	" "
4.........	$13{\cdot}1\times10^{-5}$	$22{\cdot}0\times10^{-6}$	$+22{\cdot}8\times10^{-5}$	" "
5.........	$27{\cdot}3\times10^{-5}$	$34{\cdot}2\times10^{-6}$	$+18{\cdot}7\times10^{-5}$	" "

Anticipating the results which follow, we shall find that they confirm the fact that with colloidal solutions the particles of which are positively charged, the negatively charged ions are the ones to which the coagulative action is due; consequently the amounts of electrolyte are entered always in terms of the weight of the acid radical.

It will be noticed from the table, that at first the addition of KCl produced a slight increase in the velocity, but as larger amounts were added the velocity reached a maximum and then slowly decreased. It is important to observe that in the above samples there was no sign of coagulation even at the expiration of several weeks. Two of the solutions did coagulate at the end of six weeks, but this interval is so long that this result may have been due to some ulterior cause.

b. *Potassium Sulphate.*

Similar results for this salt, a $\frac{N}{200}$ (gram-molecular) solution of which was used, are given in Table VI.

TABLE VI.

K_2SO_4 added to Copper Colloidal Solution.

No.	Grams of SO_4 per 50 ccs. Cu Sol.	Spec. Cond. at 18° C.	Velocity at 18° C.	Coagulation.
1.........	0	$5{\cdot}8\times10^{-6}$	$+25{\cdot}4\times10^{-5}$	
2.........	$3{\cdot}6\times10^{-5}$	$9{\cdot}3\times10^{-6}$	$+25{\cdot}3\times10^{-5}$	No sign.
3.........	$8{\cdot}9\times10^{-5}$	$12{\cdot}4\times10^{-6}$	$+24{\cdot}0\times10^{-5}$	„ „
4.........	$17{\cdot}8\times10^{-5}$	$18{\cdot}7\times10^{-6}$	$+21{\cdot}8\times10^{-5}$	In two weeks.
5.........	$44{\cdot}5\times10^{-5}$	$38{\cdot}5\times10^{-6}$	$+14{\cdot}4\times10^{-5}$	In two hours.
6.........	$71{\cdot}2\times10^{-5}$	$58{\cdot}3\times10^{-6}$	0	In one hour.

When more KCl and K_2SO_4 than the greatest amounts shown in the above tables was added to 50 ccs. of the colloidal solution, the conductivity became so large that the current through the liquid spoiled the velocity readings.

c. *Aluminium Sulphate.*

In similar experiments on colloidal gold and silver solutions from 18×10^{-5} to 25×10^{-5} gram of $Al_2(SO_4)_3$ per 100 ccs. of colloidal solution was sufficient to reduce the velocity of the gold and silver particles to zero. The very strong action of this salt was attributed to the trivalent aluminium ion. According to the theory then suggested, this salt should not have nearly so strong an action on the copper colloidal solution on account of the fact that the copper particle bears a positive charge, and therefore the active ion in the aluminium solution will be the SO_4. The results given in Table VII. confirm this view entirely.

Table VII.

$Al_2(SO_4)_3$ added to Copper Colloidal Solution.

No.	Grams of SO_4 per 50 ccs. Cu Sol.	Spec. Cond. at 18° C.	Velocity at 18° C.	Coagulation.
1.........	0	$7{\cdot}7\times10^{-6}$	$+23{\cdot}4\times10^{-5}$	
2.........	$6{\cdot}7\times10^{-5}$	$12{\cdot}9\times10^{-6}$	$+21{\cdot}5\times10^{-5}$	No sign.
3.........	$13{\cdot}4\times10^{-5}$	$14{\cdot}9\times10^{-6}$	$+19{\cdot}2\times10^{-5}$	*
4.........	$26{\cdot}0\times10^{-5}$	$20{\cdot}2\times10^{-6}$	$+18{\cdot}5\times10^{-5}$	*

* The two samples were not retained for coagulation observations.

It will be seen from the table that, although about 62×10^{-5} gram of aluminium sulphate was added to 100 ccs. of copper colloidal solution, there is very slight diminution of the velocity, while in none of the samples was there any immediate sign of coagulation—results in marked contrast with those obtained when the same electrolyte was added to gold and silver colloidal solutions.

d. *Potassium Phosphate.*

This salt was chosen as one representative of those possessing a trivalent acid radical. That its action on the copper is very keen is shown by the numbers in Table VIII.

Table VIII.

K_3PO_4 added to Copper Colloidal Solution.

No.	Grams of PO_4 per 50 ccs. Cu Sol.	Spec. Cond. at 18° C.	Velocity at 18° C.	Coagulation.
1.	0	$6{\cdot}5\times10^{-6}$	$+25{\cdot}4\times10^{-5}$	
2.	$1{\cdot}7\times10^{-5}$	$7{\cdot}8\times10^{-6}$	$+21{\cdot}5\times10^{-5}$	No immed. sign.
3.	$3{\cdot}5\times10^{-5}$	$8{\cdot}3\times10^{-6}$	$+16{\cdot}8\times10^{-5}$	„ „
4.	$6{\cdot}8\times10^{-5}$	$9{\cdot}9\times10^{-6}$	$+\ 3{\cdot}4\times10^{-5}$	3 to 4 hours.
5.	$10{\cdot}2\times10^{-5}$	$11{\cdot}7\times10^{-6}$	$-\ 4{\cdot}8\times10^{-5}$	In 2 hours.
6.	$15{\cdot}6\times10^{-5}$	$15{\cdot}7\times10^{-6}$	$-\ 7{\cdot}9\times10^{-5}$	In a few hours.

e. *Potassium Ferricyanide.*

The results (Table IX.) for this electrolyte, which also has a trivalent acid radical, are in complete accord with those given by the phosphate.

TABLE IX.

$K_6(FeCy_6)_2$ added to Copper Colloidal Solution.

No.	Grams of $FeCy_6$ per 50 ccs. Cu Sol.	Spec. Cond. at 18° C.	Velocity at 18° C.	Coagulation.
1.	0	$4{\cdot}3\times10^{-6}$	$+30{\cdot}4\times10^{-5}$	
2.	$7{\cdot}5\times10^{-5}$	$7{\cdot}6\times10^{-6}$	$+14{\cdot}0\times10^{-5}$	No. immed sign.
3.	$15{\cdot}0\times10^{-5}$	$9{\cdot}3\times10^{-6}$	$+3{\cdot}8\times10^{-5}$	In one hour.
4.	$22{\cdot}5\times10^{-5}$	$13{\cdot}0\times10^{-6}$	$+1{\cdot}0\times10^{-5}$	„ „
5.	$30{\cdot}0\times10^{-5}$	$18{\cdot}8\times10^{-6}$	$-1{\cdot}5\times10^{-5}$	„ „
6.	$45{\cdot}0\times10^{-5}$	$28{\cdot}6\times10^{-6}$	$-9{\cdot}1\times10^{-5}$	„ „

We see that very small quantities of either potassium phosphate or potassium ferricyanide are sufficient to reduce the velocity of the copper particles to zero and even to reverse the direction of their motion in an electric field.

5. COLLOCATION OF RESULTS.

In order the better to illustrate the relation between the number of molecules of the various electrolytes added per cc. of the copper colloidal solution and the resulting velocity of the copper particles in a given field, all of the results recorded in Tables V. to IX. inclusive are brought together in slightly different form in Table X., and illustrated in the curves in figs. 3 and 4. Column 1 gives the numbers from which the solutions may be identified in the above tables. In column 2 is given the normality, in respect of the electrolyte, of the mixture of the colloid and the electrolyte; *i. e.* the number of gram-molecules of the salt per cc. of the mixture. According to the accepted dissociation theory, we may look upon the salts in these extremely dilute solutions as being completely ionized, and so the normality as defined above will be directly proportional to the number of ionized molecules of the particular salt per cc. However,

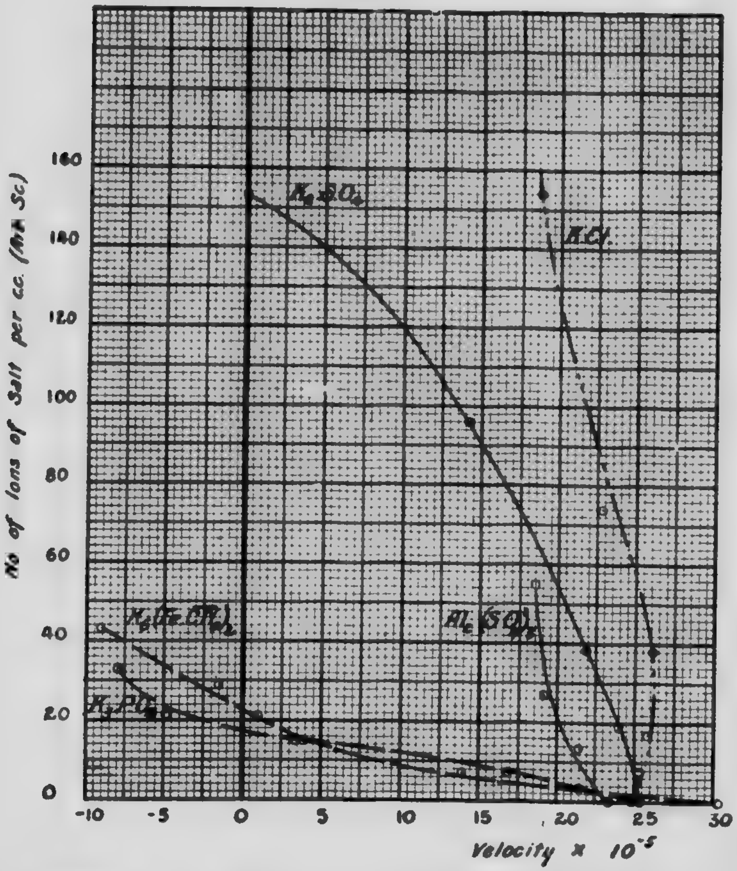
TABLE X.

Relation between the number of negative ions added per cc. to the copper colloidal solutions and the resulting velocities of the particles.

Solution.		Normality: gram-mols per cc.	Numbers proportional to the number of ions per cc.: Gram-ions/cc.	Velocity at 18° C.
KCl	1.	0	0	$+24{\cdot}9\times10^{-5}$
	2.	$17{\cdot}0\times10^{-6}$	$17{\cdot}0\times10^{-6}$	$+25{\cdot}7\times10^{-5}$
	3.	$38{\cdot}0\times10^{-6}$	$38{\cdot}0\times10^{-6}$	$+26{\cdot}2\times10^{-5}$
	4.	$74{\cdot}0\times10^{-6}$	$74{\cdot}0\times10^{-6}$	$+22{\cdot}8\times10^{-5}$
	5.	$154{\cdot}0\times10^{-6}$	$154{\cdot}0\times16^{-6}$	$+18{\cdot}7\times10^{-5}$
K_2SO_4	1.	0	0	$+25{\cdot}4\times10^{-5}$
	2.	$7{\cdot}7\times10^{-6}$	$7{\cdot}7\times10^{-6}$	$+25{\cdot}3\times10^{-5}$
	3.	$19{\cdot}2\times10^{-6}$	$19{\cdot}2\times10^{-6}$	$+24{\cdot}0\times10^{-5}$
	4.	$38{\cdot}4\times10^{-6}$	$38{\cdot}4\times10^{-6}$	$+21{\cdot}8\times10^{-5}$
	5.	$96{\cdot}0\times10^{-6}$	$96{\cdot}0\times10^{-6}$	$+14{\cdot}4\times10^{-5}$
	6.	$153{\cdot}0\times10^{-6}$	$153{\cdot}0\times10^{-6}$	$+\ 0{\cdot}0\times10^{-5}$
$Al_2(SO_4)_3$...	1.	0	0	$+23{\cdot}4\times10^{-5}$
	2.	$4{\cdot}6\times10^{-6}$	$13{\cdot}8\times10^{-6}$	$+21{\cdot}5\times10^{-5}$
	3.	$9{\cdot}2\times10^{-6}$	$27{\cdot}6\times10^{-6}$	$+19{\cdot}2\times10^{-5}$
	4.	$18{\cdot}3\times10^{-6}$	$54{\cdot}9\times10^{-6}$	$+18{\cdot}5\times10^{-5}$
K_3PO_4......	1.	0	0	$+25{\cdot}4\times10^{-5}$
	2.	$3{\cdot}6\times10^{-6}$	$3{\cdot}6\times10^{-6}$	$+21{\cdot}5\times10^{-5}$
	3.	$7{\cdot}2\times10^{-6}$	$7{\cdot}2\times10^{-6}$	$+16{\cdot}8\times10^{-5}$
	4.	$14{\cdot}4\times10^{-6}$	$14{\cdot}4\times10^{-6}$	$+\ 3{\cdot}4\times10^{-5}$
	5.	$21{\cdot}6\times10^{-6}$	$21{\cdot}6\times10^{-6}$	$-\ 4{\cdot}8\times10^{-5}$
	6.	$32{\cdot}8\times10^{-6}$	$32{\cdot}8\times10^{-6}$	$-\ 7{\cdot}9\times10^{-5}$
$K_6(FeCy_6)_2$...	1.	0	0	$+30{\cdot}4\times10^{-5}$
	2.	$3{\cdot}55\times10^{-6}$	$7{\cdot}1\times10^{-6}$	$+14{\cdot}0\times10^{-5}$
	3.	$7{\cdot}15\times10^{-6}$	$14{\cdot}3\times10^{-6}$	$+\ 3{\cdot}8\times10^{-5}$
	4.	$10{\cdot}7\times10^{-6}$	$21{\cdot}4\times10^{-6}$	$+\ 1{\cdot}0\times10^{-5}$
	5.	$14{\cdot}3\times10^{-6}$	$28{\cdot}6\times10^{-6}$	$-\ 1{\cdot}5\times10^{-5}$
	6.	$21{\cdot}4\times10^{-6}$	$42{\cdot}8\times10^{-6}$	$-\ 9{\cdot}1\times10^{-5}$

if we are to compare the efficiency of various ions in discharging the colloidal particles, we must deduce numbers directly proportional to the number of such ions per cubic centimetre. For example, taking the above definition of normality, we may look upon a 3×10^{-6} normal solution of potassium phosphate as containing the same number of molecules as the number of molecules of $K_6(FeCy_6)_2$ in a 3×10^{-6} normal solution of potassium ferricyanide. But the latter solution will contain twice the number of $FeCy_6$ ions that the former contains of PO_4 ions. Consequently in column 3 are written the numbers directly proportional to the number of acid radical ions present per cubic centimetre; of course, those numbers opposite the aluminium sulphate and the potassium ferricyanide are the only ones which will

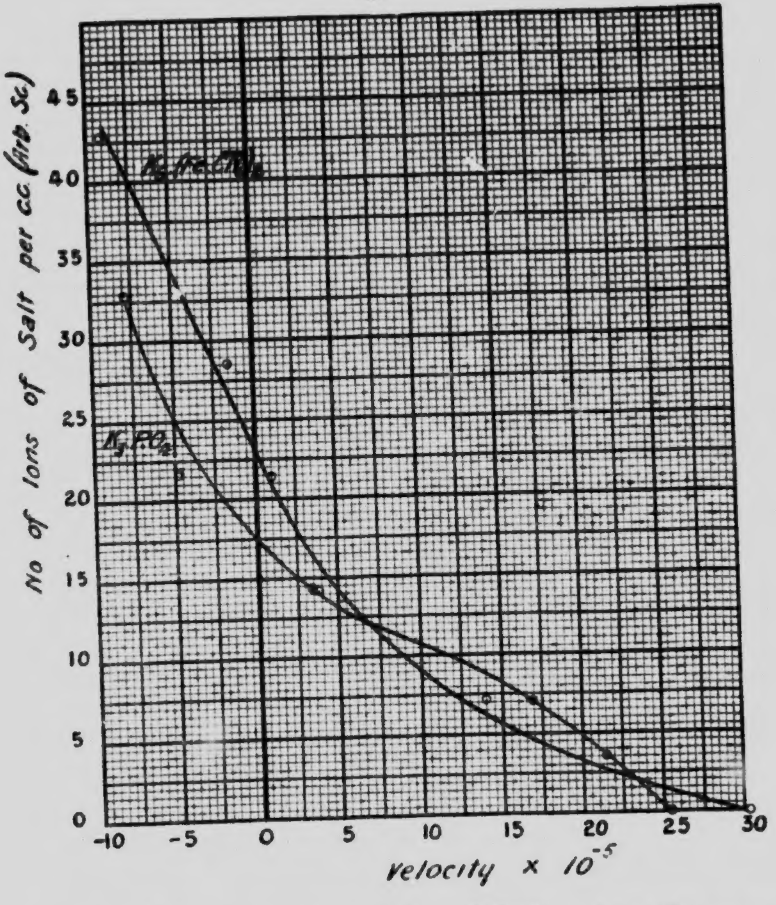
Fig. 3.



differ in the two columns. In the last column are copied the various velocities in cms./sec./volt/cm.

The curves in fig. 3 are drawn with the velocities as abscissæ and the numbers proportional to the number of ions per cc. as ordinates. The very marked overlapping of the curves for potassium phosphate and potassium ferricyanide, which are shown to larger scale in fig. 4, at once suggests

Fig. 4.



the fact that the two ions PO_4 and $FeCy_6$ have the same power of reducing the velocity of the copper particle, and, therefore, of producing the coagulation of the copper. The evidences of coagulation given in the last columns of Tables VIII. and IX. support the latter statement, as does the work of many other writers. Although the experiments on aluminium sulphate were not carried out as far as those on potassium sulphate, nevertheless the corresponding curves show a remarkable coincidence in the region common to the two curves.

These latter two curves have an additional importance in that they show that the action of the SO_4 ion is practically independent of the metal ion. Since aluminium is trivalent and potassium monovalent, if the metal ions exerted any marked influence on the copper particle we should expect these two curves to be very far apart.

Again, comparing the five curves, one has the very strongest evidence of the great differences in the powers of monovalent, divalent, and trivalent acid ions to reduce the velocity of the positively charged copper, and consequently, to produce coagulation. Examination of the curves will show that the velocity results indicate that the ratios of the powers of various acid ions to reduce the velocity of the copper particles are not very far removed from the observed ratios of the powers of the same ions to produce coagulation. These latter ratios for monovalent, divalent, and trivalent ions as found by Picton and Linder * were 1 : 35 : 1023 ; the analogous ratios suggested in accordance with Whetham's theory † of coagulation were 1 : 32 : 1024.

Some time since Duclaux published results of his work on colloids synthetically prepared by a double decomposition, as, for example, the colloidal solution of copper ferrocyanide resulting from the action of cupric chloride ($CuCl_2$) on potassium ferrocyanide. In this case he finds that the colloidal particle retains varying quantities of the potassium, to which he gives the credit for the existence of the colloidal particle. This portion of the colloidal unit he calls the "partie active," and draws the conclusion that the coagulation of the colloid is brought about through the substitution of the "partie active" by some other ions. In the course of his argument, he expresses "most formal doubts as to the exactitude of Hardy's law according to which the coagulative power of an ion is the greater, the higher its valency." The law of Hardy referred to above is based on the experimental work of Picton and Linder and others, as well as that of Hardy himself, and is uniquely supported by the theoretical contribution of Whetham. The conclusions arrived at by Duclaux seem so diametrically opposed to all this work, as to suggest the possibility that Duclaux was dealing with colloidal solutions quite different in their constitution from those upon which the above law was based. This conclusion

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* *Loc. cit.*

† 'Theory of Solution,' p. 396.

is suported by Lottermoser's criticism of Duclaux's work, in which the former constantly refers to a class of colloids which can be changed by the addition of certain electrolytes from hydrosols to hydrogels and *vice versa* ; whereas in no case have the metallic colloids at present under discussion shown that they are thus reversible.

Exception must be taken, however, to the remark of Duclaux when he says that "it is by no means evident that the immobility of a micelle in an electric field implies that the micelle does not carry a charge." Historically, the only reason we have for attributing the possession of a charge to the colloidal particle is the fact that it does move in an electric field, and, if dependence is not to be placed on this assumption, there is no ground for speaking of the particles as being charged at all. If we mean anything by the statement that a colloidal particle is positively or negatively charged, it is surely a just conclusion to say that, if the particle does not move in an electric field, it has lost its charge.

6. CONCLUSIONS.

1. For a copper colloidal solution, the particles of which are positively charged (*i. e.* move to the cathode), the influence of added electrolytes on the velocity of the particle has been determined. The electrolytes used were potassium chloride, potassium phosphate, potassium sulphate, potassium ferricyanide, and aluminium sulphate.
2. Evidence has been produced to show that it is the ion bearing a negative charge that is active in reducing the velocity.
3. This power of the negative ion depends on the valency in a way analogous to the valency relations found by Picton and Linder, and by Hardy, for the coagulative power of ions.
4. The discharging power of two negative ions of the same valency is the same.
5. Observations on the coagulation produced in each case shows that the particles coagulate when they lose their charge.

In conclusion, I wish to thank Professor J. C. McLennan for his kind assistance and encouragement at all times ; I also desire to express my indebtedness to Professor A. B. Macallum for his helpful suggestions on many occasions.

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